

# Nature inspired Synthesis of Blue Emitting Mn<sup>2+</sup>Doped ZnAl<sub>2</sub>O<sub>4</sub> Nano Ceramics

S. Ravi<sup>1</sup>, D.Prakashbabu<sup>2</sup>, S.Ponkumar<sup>3</sup>

Department of Physics, Sri Krishna Institute of Technology, Bangalore, India<sup>1</sup>

School of Physics, Reva University, Kattigenahalli, Bangalore, India<sup>2</sup>

Department of Physics, Thiruvalluvar Government Arts College, Rasipuram, India<sup>3</sup>

**ABSTRACT:** In this study ZnAl<sub>2</sub>O<sub>4</sub>: Mn<sup>2+</sup> spinel phosphor nanoparticles were prepared by one step, lowtemperature, self-propagating green-solution combustion process. The effects of doping on the structure, microstructure and luminescence of the nano phosphors were investigated. The X-ray diffraction (XRD) confirmed the formation of single-phase spinel in the investigated powders. The crystallite size and lattice constant increased as the doping level of Mn<sup>2+</sup> increased. The phosphors were excited at 370 nm (NUV) to study the PL characteristics, they exhibit strong bands centered at 465 nm corresponding to the typical <sup>4</sup>T<sub>2</sub>(G) → <sup>6</sup>A<sub>1</sub>(S) transitions.

**KEYWORDS:** solution combustion synthesis, colour tunable emission, Photoluminescence, Green synthesis.

## I. INTRODUCTION

Recently, many researchers are focusing on the synthesis of different nanocrystals with sizes ranging from 1 to 100 nm. This type of nanocrystals presents interest due to the interesting size-dependent physical, chemical, electrical, magnetic and optical properties in comparison with those of their bulk crystals [1]. Zinc aluminate (ZnAl<sub>2</sub>O<sub>4</sub>) is a widely used ceramic, electronic and catalytic material with spinel structure [2]. ZnAl<sub>2</sub>O<sub>4</sub> is suitable in thermal control coatings for spacecraft and also for ultraviolet optoelectronic devices applications [3-5]. Green electroluminescence and luminescence due to stress (mechano luminescence) have been obtained in Mn<sup>2+</sup>-doped ZnAl<sub>2</sub>O<sub>4</sub>. Recently, a bright green cathode luminescence (CL) under low excitation voltage from Mn-doped ZnAl<sub>2</sub>O<sub>4</sub> thin films prepared by spray pyrolysis have been reported by Lou et.al [6].

## II. LITERATURE SURVEY

The bandgap of ZnAl<sub>2</sub>O<sub>4</sub> nano glass ceramic is 5.2 eV, indicating its transparency for light above wavelengths 320nm. Therefore, it is widely used as a high-temperature material, optical and electronic coating material, ultra-violet photo electronic material and also as a catalyst support [6-8]. High surface area and accessible porosity are desirable properties in some applications of ZnAl<sub>2</sub>O<sub>4</sub> nano powders; for example, the catalytic properties of ZnAl<sub>2</sub>O<sub>4</sub> nano powders are largely dependent on their microstructure with a high surface area [9, 10].

The wide band gap nature of the materials is limiting it being used in production of devices for specific applications. Doping has been considered as one of the ways to alter the band gap [11]. Recently lot of works have been reported for the synthesis of simple oxides and very few reports on complex oxides using extracts of plants such as neem, alfalfa, Cinnamomum camphora, Emblica officinalis, lemon grass, tamarind, and Euphorbia tirucalli [12,13]. Although some reports are available on the production of nanophosphors using plant extracts, effective use of plant extracts in synthesis of both simple and complex oxide nanophosphors is yet to be explored. In the present work, for the first time we report the preparation of ZnAl<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup> nano powders by modified combustion method using plant extract and the effect of Mn<sup>2+</sup> concentrations on their PL properties were discussed. The structural, morphological and optical properties of these powders have been studied and the effect of Mn<sup>2+</sup> concentration on these properties has been investigated.

### III. METHODOLOGY

Starting materials used for the combustion synthesis were analar grade zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ :99.99%, Sigma Aldrich Ltd), aluminium nitrate( $\text{Al}(\text{NO}_3)_3$ :99.99%,Sigma Aldrich Ltd.) and manganese nitrate ( $\text{Mn}(\text{NO}_3)_2$ :99.99%, Merk Ltd.). Stoichiometric composition of nitrates was calculated based on the total oxidizing valences of the oxidizers and dissolved in 10 ml double distilled water, to this solution 3 ml of aloe-latex was added and mixed using magnetic stirrer for about 5 minutes to form a uniform mixture.

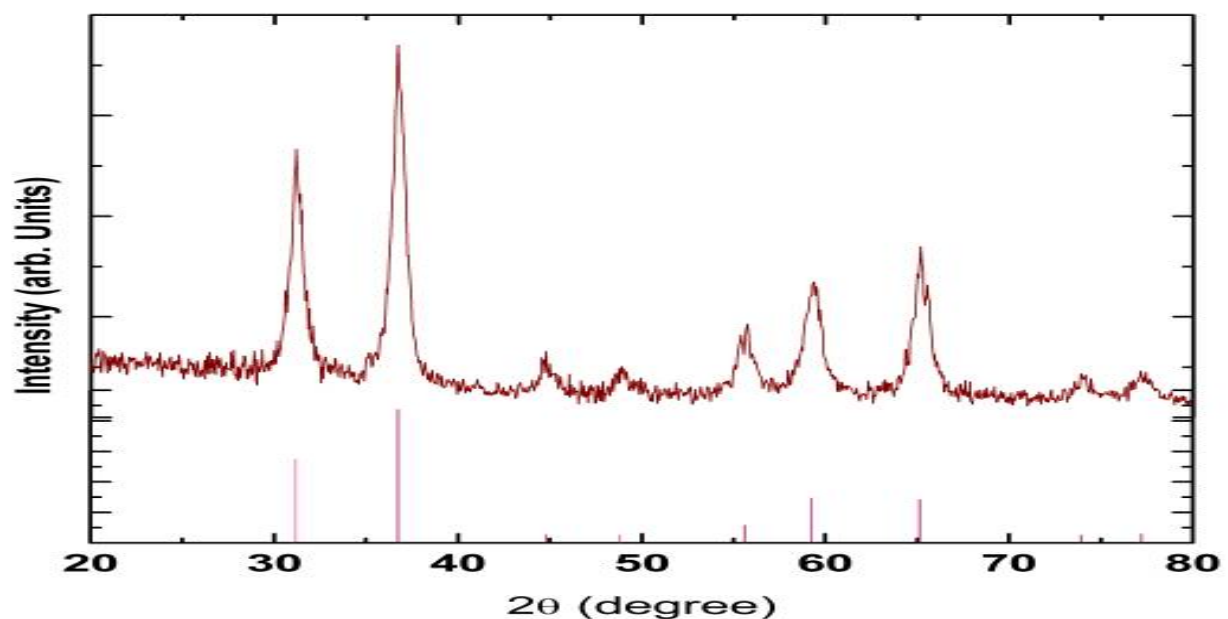
This aqueoussolution containing the redox mixture was taken in a crystalline dish and introduced in a 400°C preheated muffle furnace. The solution first got dehydrated and was ignited leaving a foam like zinc aluminate in the crystalline dish. The prepared sample was calcined at 800° C for two hours.

PXRD measurements was recordedusingPANalitical-Philips PW 1050/70fitted with Nickel – filtered Cu K $\alpha$  radiation. UV–Visible spectral study was carried out using UV–Vis spectrophotometer(ELICO SL 159 model).The photoluminescence measurement was performed on a Shimadzu (RF 510Model)spectrofluorometerwith xenon lamp as an excitation source.

### IV. SIMULATION RESULTS

The formation of crystalline phase prepared by solution combustion method was confirmed by PXRD measurement. Fig. 1 shows the powder X-ray diffraction pattern of  $\text{ZnAl}_2\text{O}_4$ :0.01 $\text{Mn}^{2+}$  and the observed pattern is in well agreement with the standard ICCD data (Card No: 05- 0669) with cell parameter „a“ = 8.059 Å. The crystallite size is estimated for the powder from the full width half maximum ( $\beta$ ) of the obtained diffracted peaks, from Debye–Scherrer,s formula [14].

$$d = k\lambda/\beta\cos\theta \quad \dots(1)$$



**Fig 1. PXRD spectra**

Where 'λ' is the wavelength of X-ray (1.542 Å) 'θ' is the Bragg angle, 'k' is the constant depends on the grain shape (0.94 for spherical particles) and β is full width at half maximum (FWHM) respectively. The estimated average

crystallite size is in the range 10– 18 nm and also the most prominent peak, revealing its peak position. It can be noticed that there is no shift in the peak position. This may be due to size matching of the Zn (137 pm) and Mn (137 pm). If a zinc atom is replaced by manganese atom there is no variation in the lattice size, because of size matching.

The band gap of samples were calculated to be 5.2 eV from Wood and Tauc plot using the UV absorption data, shown in Fig.3.

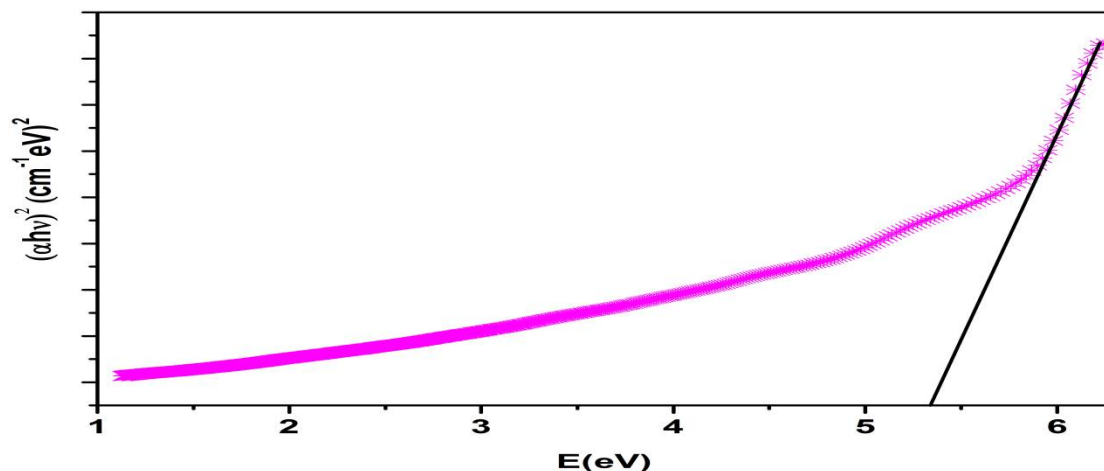


Fig 2. Wood and Tauc Plot

The photoluminescence spectra of the as formed  $\text{Zn}_{1-x}\text{Al}_2\text{O}_4: 0.01\text{Mn}$  is shown in fig.3. It shows a broad green emission peak centered at 465 nm is due to  ${}^4\text{T}_2(\text{G}) \rightarrow {}^6\text{A}_1(\text{S})$  transitions[15]. PXRD results strongly confirm that  $\text{Mn}^{2+}$  ions are located with low crystal field strength in the tetrahedral coordination of the  $\text{Zn}^{2+}$  site within the spinel structure of  $\text{ZnAl}_2\text{O}_4$ .

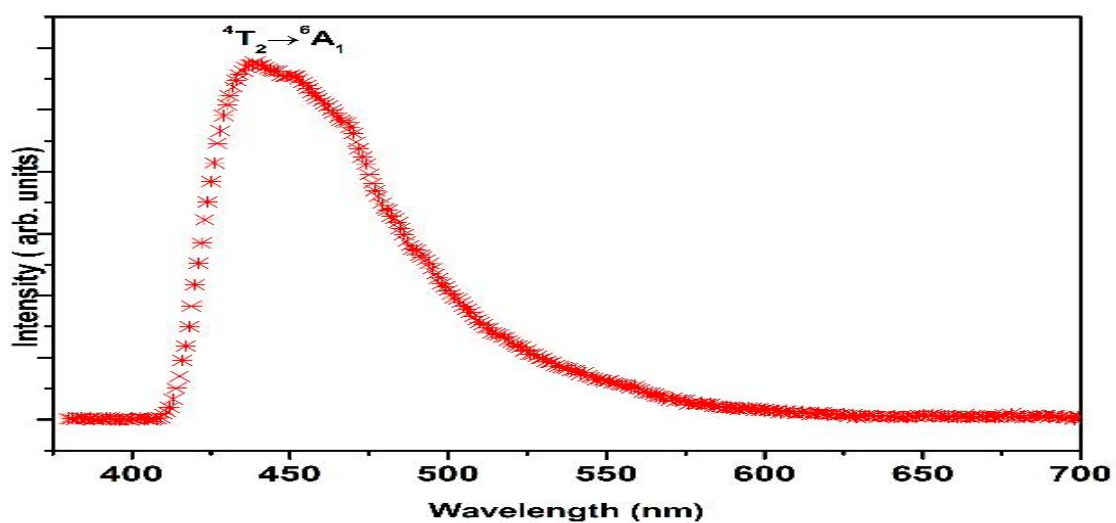


Fig.3 PL emission spectra

Most lighting specifications follows specifications of CIE chromatic colour coordinates (1931), which recognizes that the human visual system uses three primary colours: red, blue and green [16]. The x, y co-ordinate in the color space represents the color purity of the phosphors.

The color co-ordinates for 1 mol%  $\text{Mn}^{2+}$  doped  $\text{ZnAl}_2\text{O}_4$  is calculated using color calculator program, CIE coordinates of (0.12, 0.150), shown in fig.4. So, the present phosphor may find potential application for blue component in display phosphors.

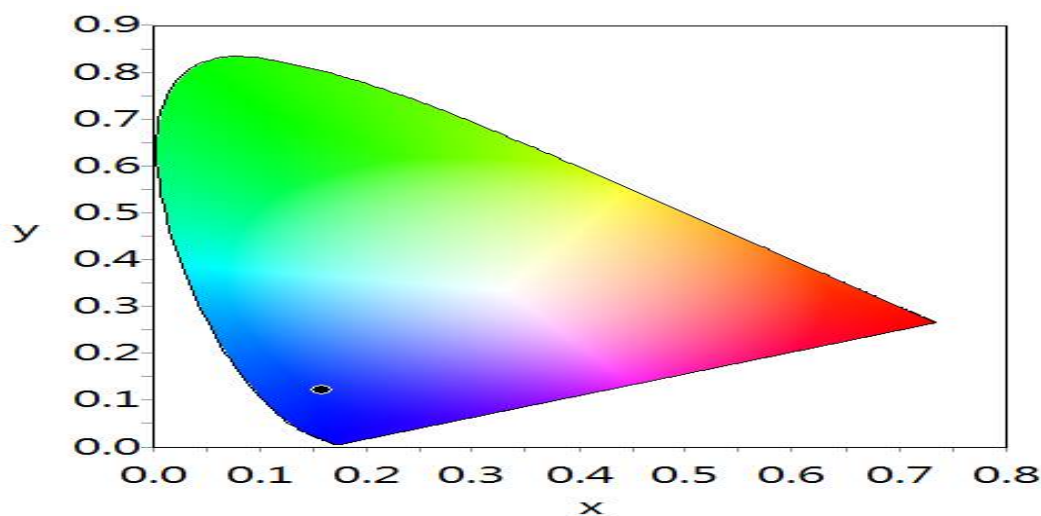


Fig.4 CIE diagram

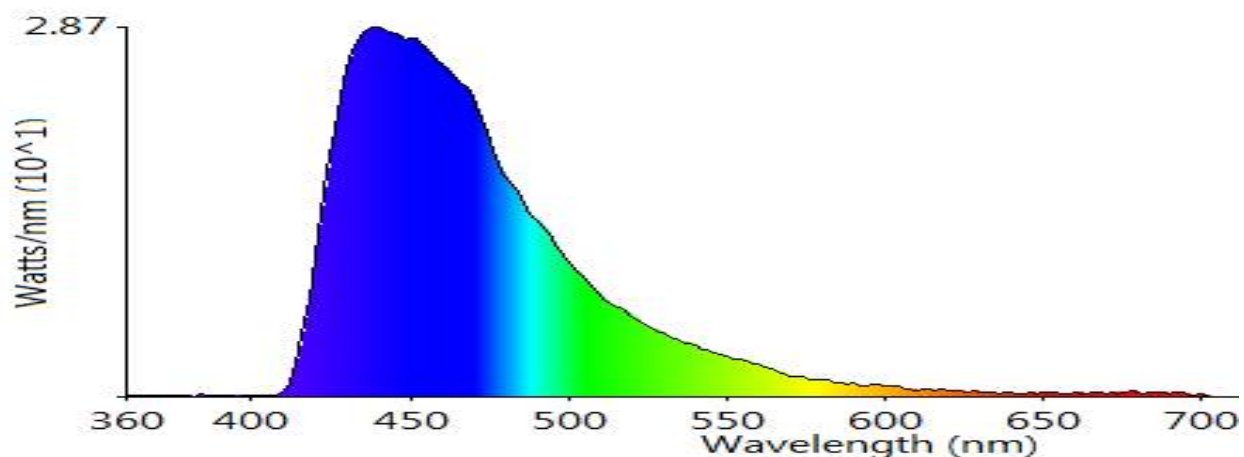


Fig.5 PL emission spectra with corresponding emission color

## V. CONCLUSION

In summary,  $\text{ZnAl}_2\text{O}_4:\text{Mn}^{2+}$  nanocrystalline powder phosphors have been synthesized by a lowtemperature initiated, self-propagating green combustion process. The PXRD patterns and FTIR studies confirm the formation of spinel structure formation. The luminescence of  $\text{Mn}^{2+}$  in  $\text{ZnAl}_2\text{O}_4$  matrix showed an intense emission in blue region

which located at 465 nm is attributed to  ${}^4T_2(G) \rightarrow {}^6A_1(S)$ . Strong and pure blue emission makes this compound suitable for three component white LEDs.

## REFERENCES

- [1] I. Miron, C Enache, I. Grozescu, "Doped Zinc Aluminate Spinel Synthesized By Hydrothermal Method" J. Nanomat. Biostructures. Vol. 7, No. 3, pp. 967 - 972 July - September 2012,.
- [2] C. L. Aguilar, M. A. Aghayan, M. A. Rodri, "Solution combustion synthesis and sintering behavior of  $CaAl_2O_4$ " J.Cer. International. 38 (2012) 395-399.
- [3] A.E. Galetti, M.F. Gomez, L.A. Arrúa, M.C. Abello, J.Appl. Catal. A: Gen. 348 (2008) 94 -102.
- [4] L.M. Chen, X.M. Sun, Y.N. Liu, K.B. Zhou, Y.D. Li, Porous  $ZnAl_2O_4$  synthesized by a modified citrate technique J. Alloys Compd. Vol.376 pp.no 257-261 (2004).
- [5] N. Guilhaume, M. Primet, J. Chem. Soc., Faraday Trans. Catalytic combustion of methane : copper oxide supported on high-specific-area spinels synthesized by a sol-gel process Issue 11 pp.no 1541-1545 (1994)
- [6] Z. Lou, J. Hao, Appl. Phys. A: Mater. Sci. & Process. Cathodoluminescent characteristics of green-emitting  $ZnAl_2O_4:Mn$  thin-film phosphors. A. 80 pp.no 151-154 (2005). W.S. Tzing, W.H. Tuan, The strength of duplex  $Al_2O_3/ZnAl_2O_4$  composite J. Mater. Sci. Lett. Vol. 15 pp 13951396 (1996).
- [7] S.K. Sampath, J.F. Cordaro, J. Am. Ceram. Soc. 81 (1998) 649-654.
- [8] T. El-Nabarawy, A.A. Attia, M.N. Alaya, Effect of thermal treatment on the structural, textural and catalytic properties of the  $ZnO-Al_2O_3$  system Mater. Lett. Vol. 24 pp. 319-325 (1995) .
- [9] OroosaSubohi, G.S. Kumar, M.M. Malik, & RajnishKurchania, Synthesis of bismuth titanate with urea as fuel by solution combustion route and its dielectric and ferroelectric properties Optik – Int. J. Light and Electron Optics, Vol.125 pp. 820-823 (2014).
- [10] R. Chandramohan, V. Dhanasekaran, R. Arumugam, J. Thirumalai, T. Mahalingam, Physical Properties Evaluation Of Annealed  $ZnAl_2O_4$  Alloy Thin Films Dig. J. Nanomaterials and Biostructures, Vol.7 pp. 1315-1325 (2012).
- [11] D. Prakashbabu, R. Hari Krishna, B. M. Nagabhushana, H. Nagabhushana, C. Shivakumara, R. P. S. Chakradar, R. Chandramohan, Low temperature synthesis of pure cubic  $ZrO_2$  nanopowder: structural and luminescence studies. J. Spectrochem. Acta. Part A: Mol. and Biomol. Spectroscopy, 122 pp. 216-22 (2014).
- [12] T. Alves, H. M. C. Andrade, R. C. D. Santos, A. B. Silvio, Transesterification Reaction Using Zinc Aluminate as Heterogeneous Catalyst and Supercritical Carbon Dioxide, Chemical Engineering Transactions Vol.32 pp. 883-888 (2013).
- [13] H. A. O. Ruonan, M. Qingyu, L. I. U. Wei, L. I. U. Hongling, Synthesis and luminescent properties of  $Eu^{3+}$  doped  $Y_2WO_6$  nanophosphors J. Rare Earths, Vol.31, pp. 864-870 (2013).
- [14] S. Farhadi, S. Panahandehjoo, Spinel-type zinc aluminate ( $ZnAl_2O_4$ ) nanoparticles prepared by the co-precipitation method: A novel, green and recyclable heterogeneous catalyst for the acetylation of amines, alcohols and phenols under solvent-free conditions Appl. Catal. A: Gen. Vol.382, pp. 293-302 (2010).
- [15] X. Song, S. Zheng, J. Zhang, W. Li, Q. Chen, B. Cao, Synthesis of monodispersed  $ZnAl_2O_4$  nanoparticles and their tribology properties as lubricant additives Mater. Res. Bull. Vol.47, pp. 4305-4310 (2012).